



Naval Research Laboratory Presents

Synthesis of Nanoparticles Using Reverse Micelles

By

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Complex Materials Section





Synthesis methods

- Physical methods
 - Ball milling
 - Pulsed laser deposition
 - Sputtering
- Chemical Methods
 - Sonochemical
 - Non-aqueous crystallization
 - Micelles



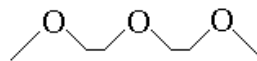


Self-Assembly Techniques

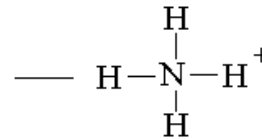
- Surfactant Methods

- Surfactants are molecules which have a hydrophobic and hydrophilic parts

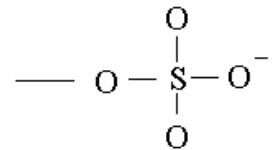
- Driven by Hydrophobic Interactions, and surface tension



*Polyethylene
glycol*



CTAB



AOT

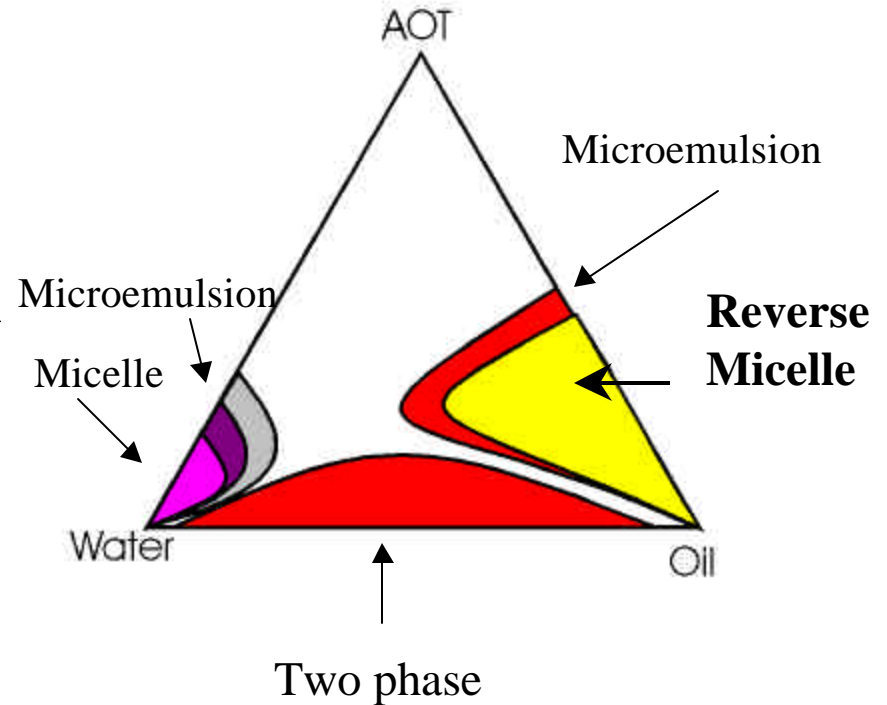




Surfactant Phase Diagram

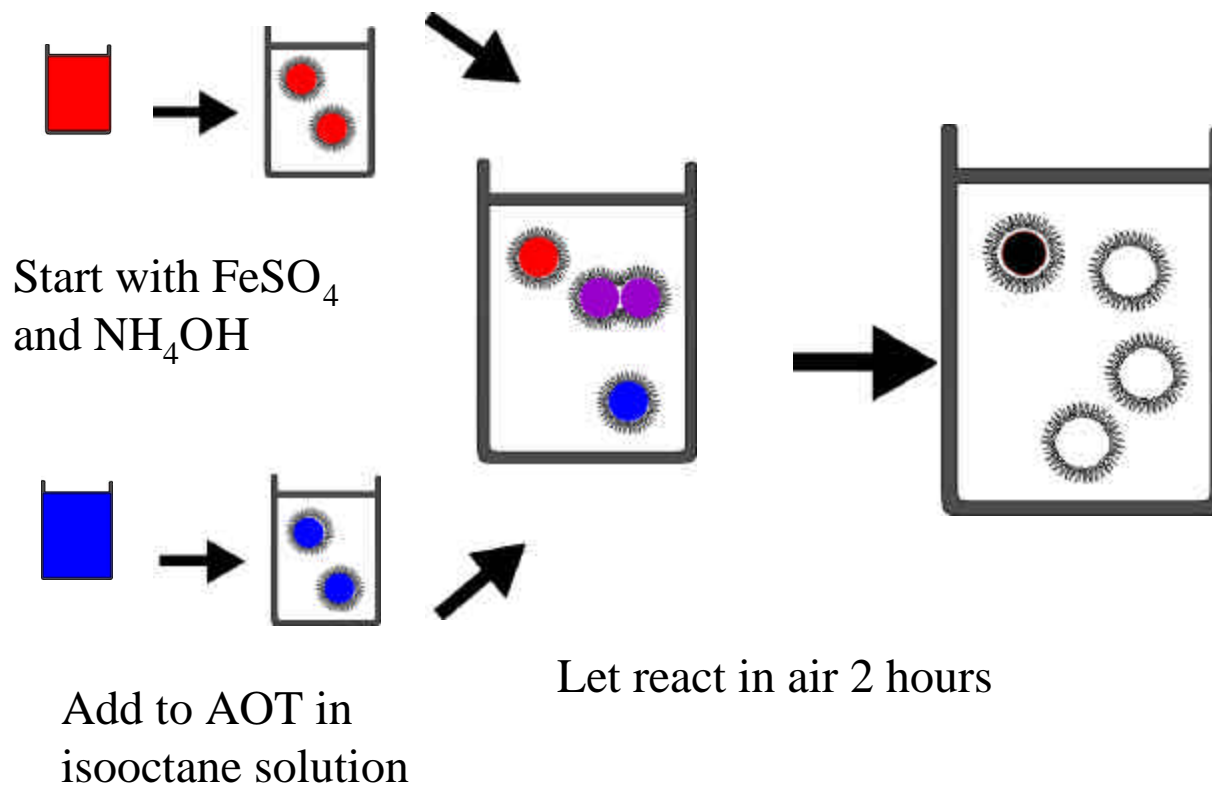
- Within micelle region, size of micelle is controlled by

$$\omega = \frac{[\text{H}_2\text{O}]}{[\text{Surfactant}]}$$





Experimental Overview





Reactions

- Ferrites
 - $\gamma\text{-Fe}_2\text{O}_3$, Fe_3O_4 , MnFe_2O_4 , CoFe_2O_4
 - LiFe_2O_4 , MgFe_2O_4 , $\text{BaFe}_{12}\text{O}_{19}$
- Perovskites
 - NaMnF_3 , KMnF_3
- Metals
 - Iron, Cobalt
 - Gold, Silver, Palladium, Platinum
 - Bismuth
- Alloy Nanoparticles
 - FePt , FePt_3 , CoPt , CoPt_3 , CoPt_5 , etc
- Semiconductors
 - CdS , CdSe , ZnSe , PbSe , etc
- Thermoelectrics
 - BiTe , BiSbTe





Advantages of Micelles

- Nanoparticle Control
- Variations in Chemical Procedure
- Variation in Processing
- Sequential Routes





Versatility

- *Variations in Chemical Procedure*
- Nanoparticle Control
 - Tailored size control
 - Narrow Size distribution
- Variation in Processing
- Sequential Routes





Variations in Chemical Procedure

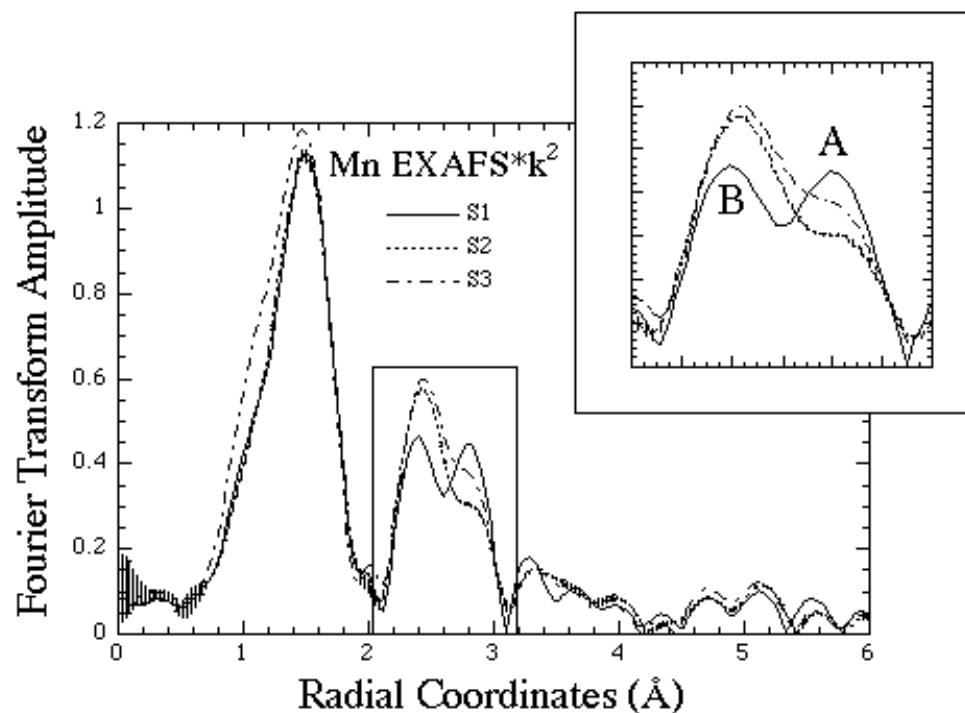
- Reactant Concentration
 - Example MFe_2O_4 where $\text{M} = \text{Mn}$ or Co
 - Lower M Concentration leads to MO shell over $\gamma\text{-Fe}_2\text{O}_3$ instead of Mixed Ferrite
- Oxidation Conditions
 - Example MnFe_2O_4
 - Use of Hydrogen Peroxide leads to change in cation distribution





Extended X-ray Absorption Fine Structure (EXAFS)

- Using H_2O_2 and a slightly elevated temperature (60°C) the cation distribution can drastically change
- Although cation distribution can be tailored, still in Spinel structure





Versatility

- *Variation in Processing*
- Nanoparticle Control
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 - Narrow Size distribution
- Variations in Chemical Procedure
 - Reactant concentrations
 - Oxidation conditions
- Sequential Routes





Variations in Processing

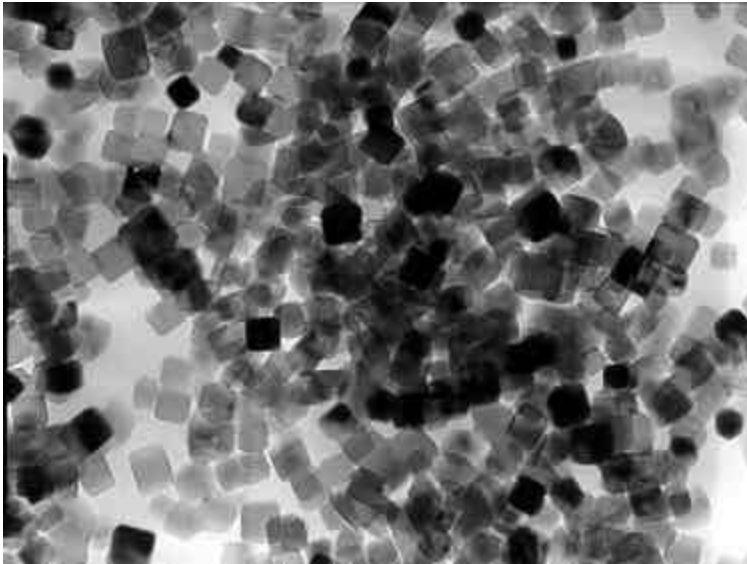
- By changing the surfactant system
 - Many in literature
- By changing reaction time
 - Example KMnF_3
 - Short reaction time cubic structures
 - Long reaction time spherical structures



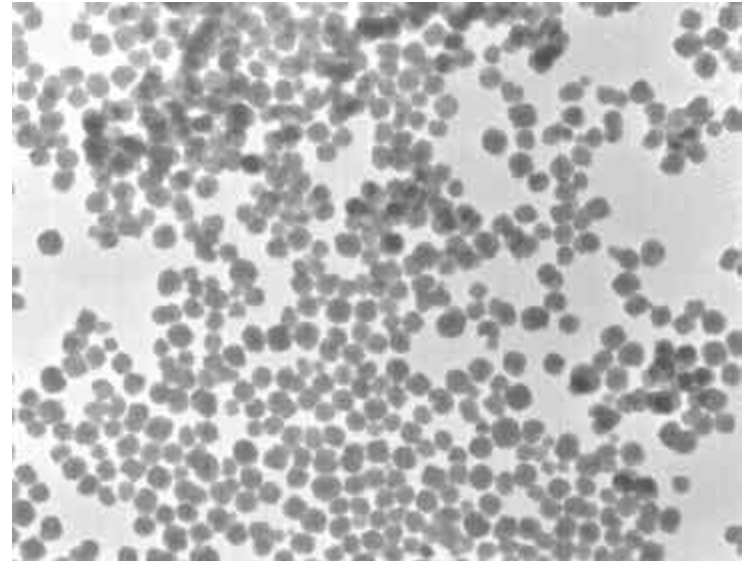


Transmission Electron Microscopy

- Reaction quenched
- Reaction time 2 hours



13 nm Particles



39 nm Particles





Versatility

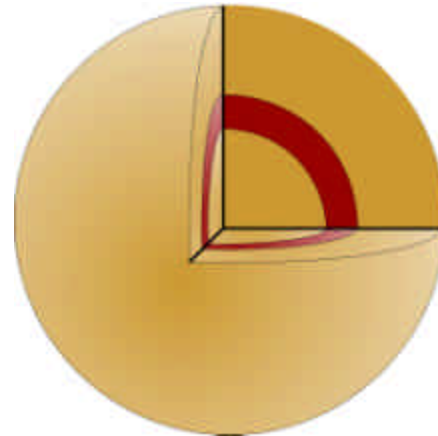
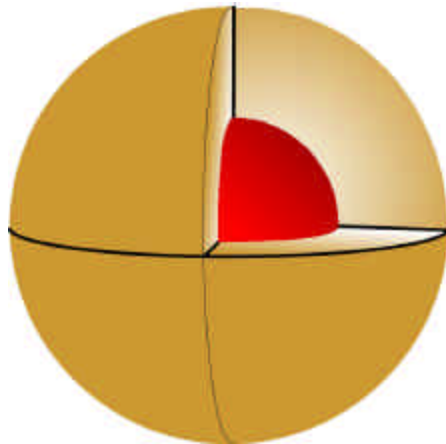
- *Sequential Routes*
- Variation in Processing
 - Changing surfactant systems
 - Changing reaction times
- Nanoparticle Control
 - Tailored size control
 - Narrow Size distribution
- Variations in Chemical Procedure
 - Reactant concentrations
 - Oxidation conditions





Sequential Synthesis

- Creating core-shell or onion structures



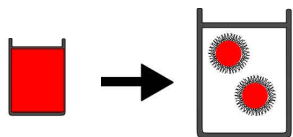
- Allows for functionality without affecting magnetic properties



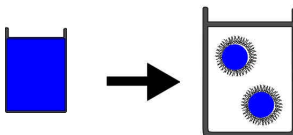


Experimental Overview

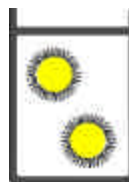
Start with FeSO_4
and NaBH_4



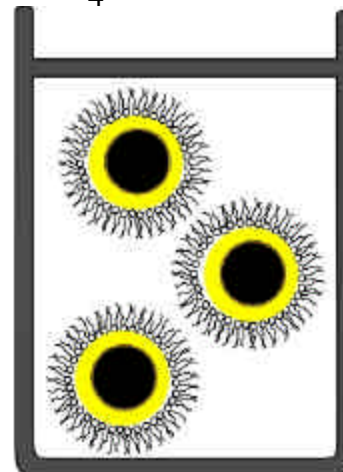
Using CTAB,
Octane, and
Butanol



React for 2 hours
to form Iron



Add HAuCl_4 and
additional NaBH_4

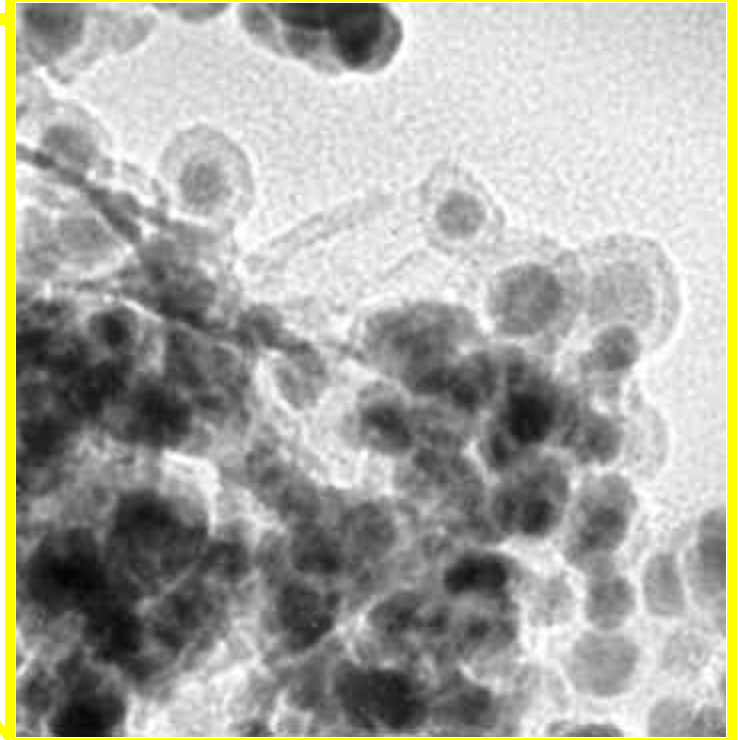
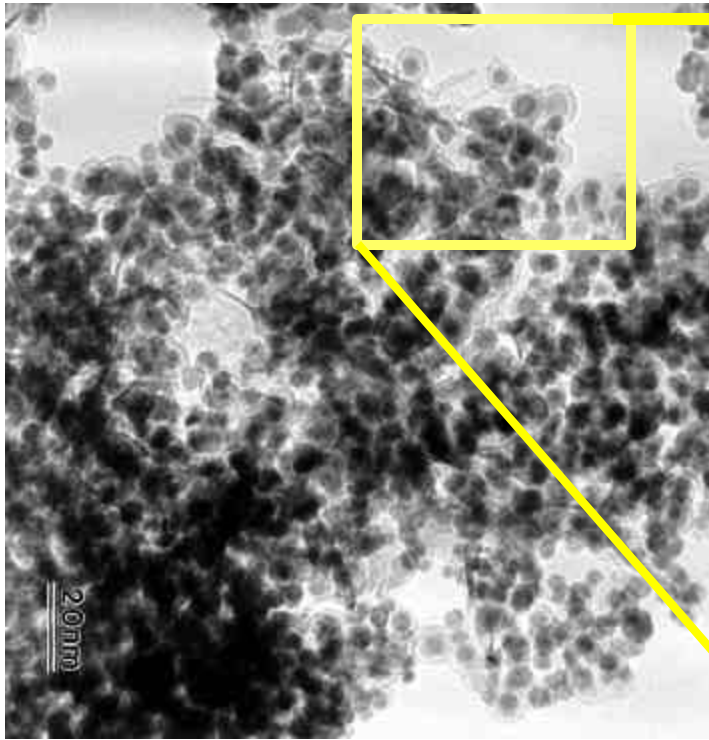


Fe acts as nucleation source
for formation of core-shell
particles



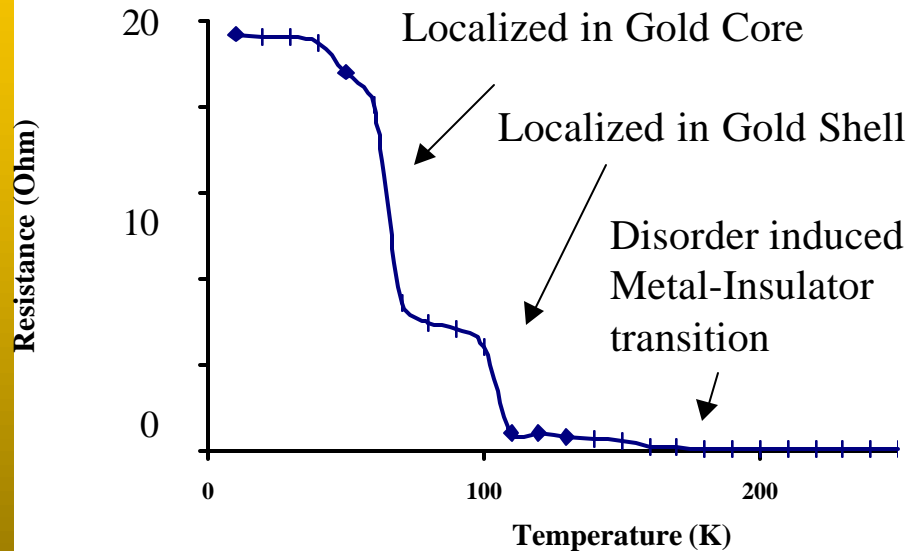


Transmission Electron Microscopy



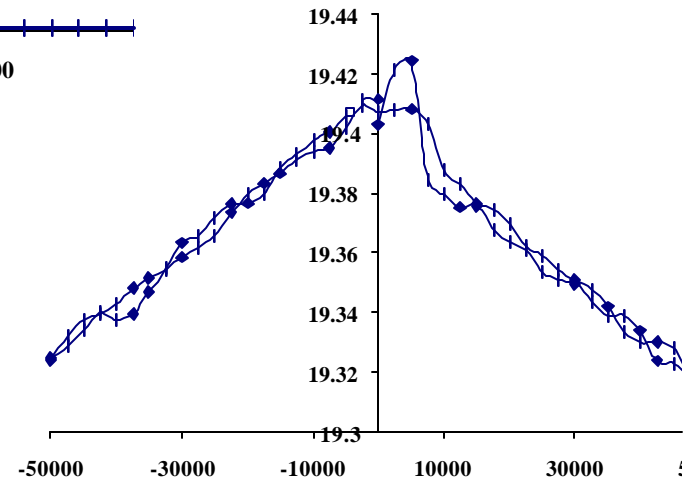


Resistivity of nano-onions



Magnetoresistance measurements were taken using the four-point method on a compressed pellet

Samples display a 400% increase in resistance below blocking temperature, and a 1% negative MR vs. Field at 10K





Applications

- Communication
 - power electronics
 - high frequency applications
- Medical
 - therapeutics
 - diagnostics
- Self-assembled structures
- Catalysis





Communication Applications

- Power Supplies
- High frequency filters
- Inductors





Medical therapeutics

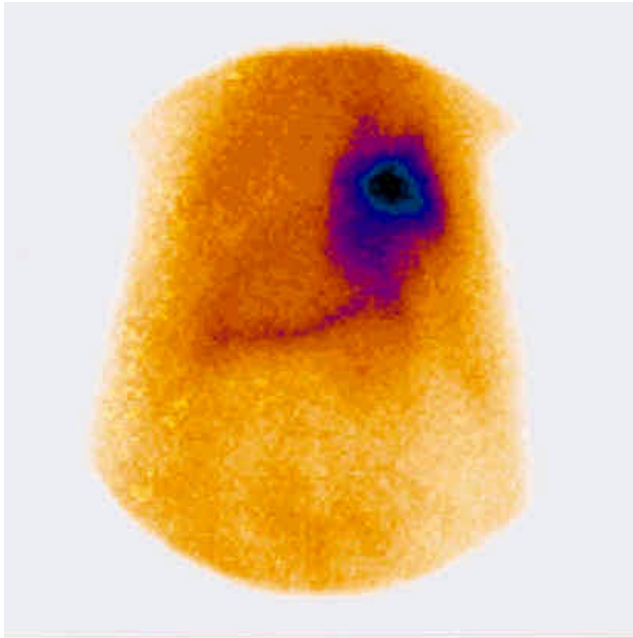
- Targeted drug delivery
- Hyperthermic treatment





Medical diagnostics

- Imaging



- Optical Bar Codes



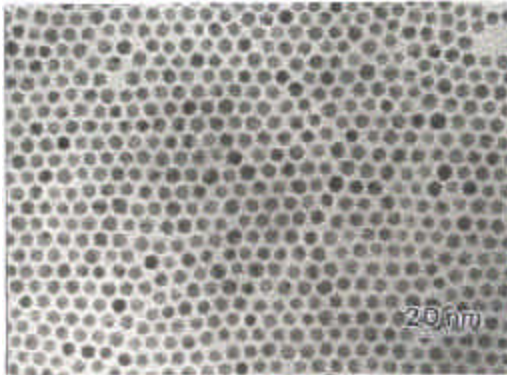
A family of Qdot particles can be made to emit a full spectrum of colors when excited with a single excitation source.



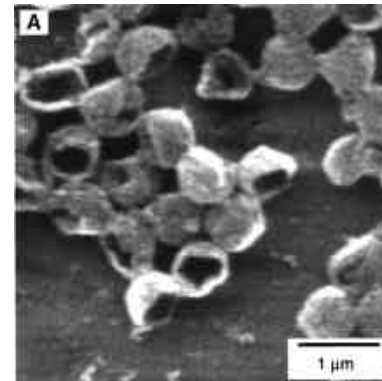


Self-assembled Structures

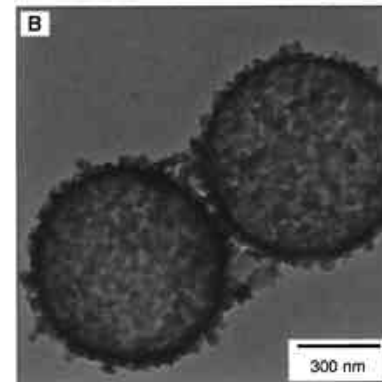
- Au, FePt



- Hollow spheres



SiO₂ grown
on PS.





Conclusion

- There is a rapidly growing need for nanostructured materials which are usable for nearly all applications
- Micelle methods are useful for synthesizing many of these materials in 5-40 nm range
- ❖ I would like to acknowledge my co-workers both at NRL and UNO who helped with this work

